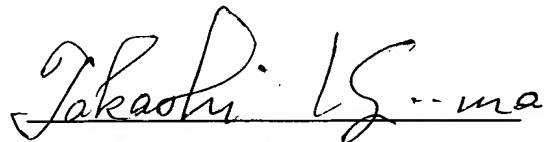




# C E R T I F I C A T I O N

I, Takashi KOJIMA of Ginza Ohtsuka Bldg., 2F, 16-12, Ginza 2-chome, Chuo-ku, Tokyo, Japan, hereby certify that I am the translator of the accompanying certified official copy of the documents in respect of an application for a patent filed in Japan on the 4th of February, 2000 and of the official certificate attached thereto, and certify that the following is a true and correct translation to the best of my knowledge and belief.

Dated this 7th day of June, 2004

  
Takashi KOJIMA

(Translation)



PATENT OFFICE  
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following application as filed with this Office.

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2000-027719

[SPECIFICATION]

[TITLE OF THE INVENTION] Undercoating Composition and  
Coating Method

5 [CLAIMS]

[Claim 1] An undercoating composition comprising an organic copolymer comprising (A) a UV-absorbing benzotriazole based vinyl monomer, (B) an alkoxysilyl group-containing vinyl monomer, and (C) another  
10 copolymerizable monomer, the alkoxysilyl group-containing vinyl monomer accounting for 0.1 to 50% by weight of the copolymer.

[Claim 2] The undercoating composition of claim 1, further comprising 0.1 to 10 parts by weight of a photo-stabilizer  
15 having at least one cyclic hindered amine structure in a molecule, per 100 parts by weight of said organic copolymer.

[Claim 3] The undercoating composition of claim 1 wherein said copolymer contains 0.1 to 10% by weight of an acrylic monomer having a cyclic hindered amine base  
20 photo-stabilizing group as component (C).

[Claim 4] The undercoating composition of any one of claims 1 to 3, further comprising 0.1 to 50 parts by weight of a compound containing a nitrogen atom and an alkoxysilyl group in one molecule, per 100 parts by weight of said  
25 organic copolymer.

[Claim 5] The undercoating composition of claim 4 wherein the compound containing a nitrogen atom and an alkoxysilyl group in one molecule is a compound containing at least one nitrogen atom and at least two alkoxysilyl groups in one  
30 molecule.

[Claim 6] A method for coating a plastic substrate with a weather and abrasion-resistant coating, comprising the steps of:

(1) applying an organic solvent solution of the  
35 undercoating composition of any one of claims 1 to 5 onto a plastic substrate,

(ii) evaporating the organic solvent and curing the coating,

(iii) applying an organopolysiloxane composition onto the primer coat, said organopolysiloxane composition comprising a hydrolyzate or co-hydrolyzate of an organoxysilane of the following general formula (1):



wherein  $R^4$  is selected from the class consisting of a alkyl group, aryl group, halogenated alkyl group, halogenated aryl group and alkenyl group of 1 to 10 carbon atoms, and an organic group having an epoxy, (meth)acryloxy, mercapto, amino or cyano group,  $R^5$  is hydrogen or an organic group of 1 to 10 carbon atoms, and m is equal to 0, 1 or 2, and

(iv) heating the coating of the organopolysiloxane composition for curing.

[Claim 7] The method for coating a plastic substrate with a weather and abrasion-resistant coating of claim 6 wherein said organopolysiloxane composition further contains colloidal silica.

[Claim 8] The method for coating a plastic substrate with a weather and abrasion-resistant coating of claim 6 or 7 wherein the plastic substrate is comprised of a polycarbonate resin.

[Claim 9] The method for coating with a weather and abrasion-resistant coating of claim 8 wherein the polycarbonate resin is transparent.

#### [DETAILED EXPLANATION OF THE INVENTION]

[0001]

#### [Technical Field of the Invention]

This invention relates to undercoating compositions for forming silicone coatings which are mar and weather-resistant protective coatings on plastic substrates currently often used as structural members instead of glass in building and vehicle windows, instrument cover, and the like, and a method of coating with the use of the composition.

[0002]

[Prior Art and Problem to be Solved by the Invention]

As glazing substitutes, shatterproof or highly shatter resistant transparent materials have been widely utilized for these decades. For example, plastic substrates, especially polycarbonate resins have superior transparency, impact resistance and heat resistance and are currently used as structural members instead of glass in a variety of applications including building and vehicle windows and instrument covers.

[0003]

The polycarbonate resins, however, are inferior to glass in surface properties such as mar resistance and weather resistance. It is desired to improve the surface properties of polycarbonate resin parts. Nowadays, polycarbonate resin parts for use as vehicle windows and acoustic barrier walls along highways are required to withstand more than 10 years of weathering.

[0004]

Known means for improving the weather resistance of polycarbonate resin parts include the lamination of a weather resistant acrylic resin film on the surface of a polycarbonate resin substrate and the formation of a ultraviolet absorber-containing resin layer on the resin surface, for example, by co-extrusion.

[0005]

For improving the mar resistance of polycarbonate resin parts, it is known to coat thermosetting resins such as polyorganosiloxanes and melamine resins and to coat photo-curable resins such as polyfunctional acrylic resins.

[0006]

As to the manufacture of transparent articles having both weather resistance and mar resistance, JP-A 56-92059 and JP-A 1-149878 disclose ultraviolet-absorbing transparent substrates having a primer layer loaded with a large amount of UV-absorber added and a protective coating of colloidal

silica-containing polysiloxane paint overlying the primer layer.

[0007]

However, several problems arise with this approach.

5 The addition of a large amount of UV-absorber to an undercoat can adversely affect the adhesion to the substrate or the protective layer of colloidal silica-containing polysiloxane coating agent applied on the surface of an undercoat. During heat curing step, the UV-absorber can  
10 volatilize off. On outdoor use over a long period of time, the UV-absorber will gradually bleed out, causing whitening. From the mar resistance standpoint, it is impossible to add a large amount of UV-absorber to the protective coating of colloidal silica-containing polysiloxane.

15 [0008]

It is also known from JP-A 6-299132, 7-90184 and 10-25434 that a copolymer of a benzotriazole based UV-absorbing vinyl monomer or a benzophenone based UV-absorbing vinyl monomer with another vinyl monomer  
20 copolymerizable therewith is used in tackifier compositions, light and chemical-resistant synthetic resins, and powder paint resins for the purpose of improving weather resistance. However, the use of such UV-absorbing copolymers in a primer or undercoat layer is unknown.  
25 Undesirably, the use of such UV-absorbing copolymers adversely affects the adhesion to the substrate and to the protective coating of colloidal silica-containing polysiloxane paint to be applied on the primer layer.

[0009]

30 Moreover, it is known from JP-A 8-151415 that a mixture of a benzotriazole based UV-absorbing vinyl monomer or a benzophenone based UV-absorbing vinyl monomer and another vinyl monomer copolymerizable therewith is used in coating compositions which are effective for forming  
35 protective coatings on surfaces of synthetic resins. Since these protective coatings are based on vinyl polymers, their mar resistance is limited.



[0010]

Accordingly, an object of the invention is to provide an undercoating composition for forming a protective coating having improved mar and weather resistance without the above problems, and a method of coating with the use of the composition.

[0011]

[Means for Solving the Problem and Embodiment of the Invention]

10 The present inventors have earnestly studied in order to attain the above object. As a result, it has been found that the above-described problems can be overcome by an undercoating composition using an organic copolymer comprising (A) a benzotriazole base UV-absorbing vinyl  
15 monomer, (B) a vinyl monomer containing an alkoxysilyl group, and (C) another monomer copolymerizable therewith, the vinyl monomer containing an alkoxysilyl group accounting for 0.1 to 50% by weight of the copolymer. Preferably an acrylic monomer having a cyclic hindered amine base  
20 photo-stabilizing group is used as the other monomer (C) in an amount of 0.1 to 10% by weight of the copolymer. The undercoating composition may further contain, per 100 parts by weight of the organic copolymer, 0.1 to 50 parts by weight a compound containing a nitrogen atom and an  
25 alkoxysilyl group in one molecule.

[0012]

The inventors sought for an undercoating composition capable of improving the adhesion and weather resistance of molded parts of thermoplastic resins such as polycarbonate  
30 which are subsequently coated with an organopolysiloxane coating. When the above organic copolymer, in which benzotriazole base UV-absorbing groups are fixed to the polymer backbone through chemical bonds, is used in the primer coating composition, the organic copolymer does not  
35 migrate to the surface, eliminates the whitening phenomenon of outer appearance, is not dissolved in water and solvents. The initial loading of the organic copolymer is retained

over a long period of time, and the UV-absorbing effect declines little with the lapse of time. Even on heat curing treatment at elevated temperature, the UV-absorber does not volatilize off the coating. The copolymer is so compatible  
5 with other components in the undercoating composition that a large amount of the copolymer may be added without detracting from the transparency and adhesion of the undercoating composition to the substrate or the protective coating.

10 [0013]

Further, since the vinyl monomer containing an alkoxysilyl group is used, alkoxysilyl groups are introduced into the undercoating layer to provide the undercoating layer with a reactivity with a protective coating layer to  
15 be applied thereon, thereby improving adhesion. This, combined with crosslinking among alkoxysilyl groups, contributes to improvements in heat resistance and durability.

[0014]

20 When a compound containing a nitrogen atom and an alkoxysilyl group in one molecule, preferably a compound containing at least one nitrogen atom and at least two alkoxysilyl groups in one molecule is added to the organic copolymer, the undercoating layer is given water-proof  
25 adhesion. The compound crosslinks with alkoxysilyl groups in the organic copolymer to densify the undercoating and serves to fix the photo-stabilizer and other optional additives within the undercoating layer. The copolymer can introduce a large amount of UV-absorbing groups in the  
30 primer coating layer while maintaining various useful properties, and eliminates the addition of or reduces the amount of a UV-absorber in an organopolysiloxane base overcoat which UV-absorber can be a detrimental factor to the mar resistance of the overcoat.

35 [0015]

Accordingly, the present invention provides the following undercoating composition and coating method.

[I] An undercoating composition comprising an organic copolymer comprising (A) a UV-absorbing benzotriazole based vinyl monomer, (B) an alkoxysilyl group-containing vinyl monomer, and (C) another copolymerizable monomer, the alkoxysilyl group-containing vinyl monomer accounting for 0.1 to 50% by weight of the copolymer.

[II] The undercoating composition further comprising 0.1 to 10 parts by weight of a photo-stabilizer having at least one cyclic hindered amine structure in a molecule, per 100 parts by weight of said organic copolymer.

[III] The undercoating composition wherein said copolymer contains 0.1 to 10% by weight of an acrylic monomer having a cyclic hindered amine base photo-stabilizing group as component (C).

[IV] The undercoating composition further comprising 0.1 to 50 parts by weight of a compound containing a nitrogen atom and an alkoxysilyl group in one molecule, per 100 parts by weight of said organic copolymer.

[V] The undercoating composition wherein the compound containing a nitrogen atom and an alkoxysilyl group in one molecule is a compound containing at least one nitrogen atom and at least two alkoxysilyl groups in one molecule.

[VI] A method for coating a plastic substrate with a weather and abrasion-resistant coating, comprising the steps of:

(i) applying an organic solvent solution of the undercoating composition onto a plastic substrate,

(ii) evaporating the organic solvent and curing the coating,

(iii) applying an organopolysiloxane composition onto the primer coat, said organopolysiloxane composition comprising a hydrolyzate or co-hydrolyzate of an organoxsilane of the following general formula (1):



wherein  $R^4$  is selected from the class consisting of a alkyl group, aryl group, halogenated alkyl group, halogenated aryl

group and alkenyl group of 1 to 10 carbon atoms, and an organic group having an epoxy, (meth)acryloxy, mercapto, amino or cyano group, R<sup>5</sup> is hydrogen or an organic group of 1 to 10 carbon atoms, and m is equal to 0, 1 or 2, and

(iv) heating the coating of the organopolysiloxane composition for curing.

[VII] The method wherein said organopolysiloxane composition further contains colloidal silica.

[0016]

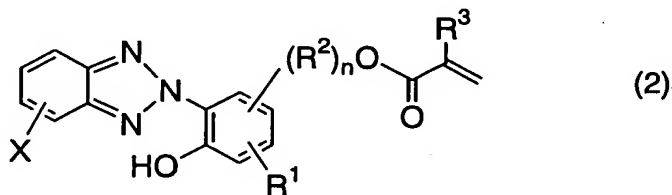
The following is the detailed description of the invention.

The undercoating composition of the present invention comprises as essential components (A) a UV-absorbing benzotriazole based vinyl monomer, (B) an alkoxysilyl group-containing vinyl monomer, and (C) another copolymerizable monomer, the alkoxysilyl group-containing vinyl monomer accounting for 0.1 to 50% by weight of the copolymer.

[0017]

The benzotriazole based UV-absorbing vinyl monomer (A) used herein is not critical as long as it has at least one benzotriazole based UV-absorbing group and at least one vinyl group in a molecule. Typical are compounds of the general formula (2).

[0018]



Herein, X is hydrogen or chlorine. R<sup>1</sup> is hydrogen, methyl or a tertiary alkyl group of 4 to 8 carbon atoms. R<sup>2</sup> is a straight or branched alkylene group of 2 to 10 carbon atoms. R<sup>3</sup> is hydrogen or methyl. The letter n is equal to 0 or 1.

[0019]

In formula (2), examples of the tertiary C<sub>4-8</sub> alkyl group represented by R<sup>1</sup> include tert-butyl, tert-pentyl,

tert-hexyl, tert-heptyl, tert-octyl and di-tert-octyl. Examples of the straight or branched C<sub>2-10</sub> alkylene group represented by R<sup>2</sup> include ethylene, trimethylene, propylene, tetramethylene, 1,1-dimethyltetramethylene, butylene, octylene, and decylene, with ethylene and propylene being preferred.

[0020]

Illustrative, non-limiting, examples of the compound of formula (2) include

- 2-(2'-hydroxy-5'-methacryloxyphenyl)-2H-benzotriazole,  
2-(2'-hydroxy-3'-tert-butyl-5'-methacryloxymethylphenyl)-2H-benzotriazole,  
2-[2'-hydroxy-5'-(2-methacryloxyethyl)phenyl]-2H-benzotriazole,  
2-[2'-hydroxy-5'-(2-acryloxyethyl)phenyl]-2H-benzotriazole,  
2-[2'-hydroxy-3'-tert-butyl-5'-(2-methacryloxyethyl)phenyl]-5-chloro-2H-benzotriazole, and  
2-[2'-hydroxy-3'-methyl-5'-(8-acryloxyoctyl)phenyl]-2H-benzotriazole.

[0021]

- The benzotriazole based UV-absorbing vinyl monomer may be used alone or in admixture of two or more.

[0022]

- The content of the benzotriazole based UV-absorbing vinyl monomer (A) in the organic copolymer is preferably 0.1 to 50%, and more preferably 3 to 40% by weight based on the copolymer composition when the compatibility of the resulting organic polymer with other primer constituents and the weather resistance of the resulting primer coating composition are taken into account. Copolymers with more than 50 wt% of the vinyl monomer (A) may become less compatible with other constituents of the primer coating composition and is uneconomical. Less than 0.1 wt% may fail to provide the desired weather resistance.

[0023]

- In the organic copolymer, the alkoxysilyl group-containing vinyl monomer (B) accounts for 0.1 to 50% by weight based on the copolymer composition. Less than 0.1

wt% of the vinyl monomer (B) fails to improve heat resistance and durability. Copolymers with more than 50 wt% of the vinyl monomer (B) becomes too hard to provide adhesion.

5 [0024]

The alkoxysilyl group-containing vinyl monomer (B) used herein is not critical as long as it has at least one alkoxysilyl group and at least one vinyl group in a molecule. Typical are compounds of the general formula (3).

10



Herein,  $R^6$  is a polymerizable unsaturated group,  $R^7$  is a straight or branched alkylene group of 1 to 10 carbon atoms,  $R^8$  and  $R^9$ , which may be the same or different, are alkyl groups of 1 to 6 carbon atoms, and L is an integer of 1 to 3.

[0025]

In formula (3), exemplary polymerizable unsaturated groups represented by  $R^6$  are vinyl, vinyloxy, (meth)acrylic, (meth)acryloyloxy, and styryl. Examples of straight or branched  $C_{1-10}$  alkylene group represented by  $R^7$  include methylene, ethylene, trimethylene, propylene, tetramethylene, 1,1-dimethyltetramethylene, butylene, octylene, and decylene. Examples of the  $C_{1-6}$  alkyl group represented by  $R^8$  and  $R^9$  are methyl, ethyl, propyl, butyl, pentyl and hexyl.

[0026]

As the alkoxysilyl group-containing vinyl monomer (B), exemplary (meth)acrylic functional monomers include

- 3-methacryloxypropyltrimethoxysilane,
- 3-methacryloxypropyltriethoxysilane,
- 3-methacryloxypropylmethyldimethoxysilane,
- 3-methacryloxypropylmethyldiethoxysilane,
- 3-acryloxypropyltrimethoxysilane,
- 3-acryloxypropyltriethoxysilane,
- 3-acryloxypropylmethyldimethoxysilane,
- 3-acryloxypropylmethyldiethoxysilane,

3-methacryloxymethyltrimethoxysilane,  
3-methacryloxymethyltriethoxysilane,  
3-methacryloxymethylmethyldimethoxysilane,  
3-methacryloxymethylmethyldiethoxysilane,  
5 3-acryloxymethyltrimethoxysilane,  
3-acryloxymethyltriethoxysilane,  
3-acryloxymethylmethyldimethoxysilane, and  
3-acryloxymethylmethyldiethoxysilane. Of these,  
3-methacryloxypropyltrimethoxysilane and  
10 3-methacryloxypropylmethyldimethoxysilane are preferred for  
ease of handling, crosslinked density and reactivity.

[0027]

Examples of the alkoxysilyl group-containing vinyl  
monomer are vinyltrimethoxysilane, vinyltriethoxysilane,  
15 vinyltris(2-methoxyethoxy)silane,  
vinylmethyldimethoxysilane, vinylmethyldiethoxysilane,  
vinylmethylbis(2-methoxyethoxy)silane,  
3-vinyloxypropyltrimethoxysilane,  
3-vinyloxypropyltriethoxysilane,  
20 3-vinyloxypropylmethyldimethoxysilane,  
3-vinyloxypropylmethyldiethoxysilane,  
styrylethyltrimethoxysilane, and styryltrimethoxysilane. Of  
these, vinyltrimethoxysilane, vinyltriethoxysilane, and  
3-vinyloxypropyltrimethoxysilane are preferred for ease of  
25 handling and reactivity.

[0028]

The other monomers (C) copolymerizable with the  
foregoing monomers include acrylic monomers having a cyclic  
hindered amine structure, (meth)acrylates,  
30 (meth)acrylonitrile, (meth)acrylamides, alkyl vinyl ethers,  
alkyl vinyl esters, styrene and derivatives thereof.

[0029]

Examples of suitable acrylic monomers having a cyclic  
hindered amine structure are  
35 2,2,6,6-tetramethyl-4-piperidinyl methacrylate and  
1,2,2,6,6-pentamethyl-4-piperidinyl methacrylate. These  
photo-stabilizers may be used in admixture of two or more.

[0030]

Examples of suitable (meth)acrylates and derivatives thereof include

(meth)acrylates of monohydric alcohols such as

5 methyl (meth)acrylate, ethyl (meth)acrylate,  
n-propyl (meth)acrylate, isopropyl (meth)acrylate,  
n-butyl (meth)acrylate, isobutyl (meth)acrylate,  
sec-butyl (meth)acrylate, t-butyl (meth)acrylate,  
n-pentyl (meth)acrylate, isopentyl (meth)acrylate,  
10 n-hexyl (meth)acrylate, isohexyl (meth)acrylate,  
n-heptyl (meth)acrylate, isoheptyl (meth)acrylate,  
2-ethylhexyl (meth)acrylate, n-octyl (meth)acrylate,  
isooctyl (meth)acrylate, n-nonyl (meth)acrylate,  
isononyl (meth)acrylate, n-decyl (meth)acrylate,  
15 isodecyl (meth)acrylate, n-undecyl (meth)acrylate,  
n-dodecyl (meth)acrylate, palmityl (meth)acrylate,  
stearyl (meth)acrylate, cyclohexyl (meth)acrylate,  
4-methylcyclohexyl (meth)acrylate,  
4-t-butylcyclohexyl (meth)acrylate, and  
20 benzyl (meth)acrylate;

(meth)acrylates of alkoxy(poly)alkylene glycols such as 2-methoxyethyl (meth)acrylate,  
2-methoxybutyl (meth)acrylate, 3-methoxypropyl (meth)acrylate,  
2-methoxybutyl (meth)acrylate, 3-methoxybutyl (meth)acrylate,  
25 4-methoxybutyl (meth)acrylate, methoxypolyethylene glycol  
(meth)acrylate (e.g., the number of ethylene glycol units is 2 to 20), and methoxypolypropylene glycol (meth)acrylate (e.g., the number of propylene glycol units is 2 to 20);

mono(meth)acrylates of polyhydric alcohols such as

30 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate,  
3-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate,  
3-hydroxybutyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate,  
glycerin mono(meth)acrylate, pentaerythritol mono(meth)acrylate,  
polyethylene glycol mono(meth)acrylate (e.g., the number of  
35 ethylene glycol units is 2 to 20), and  
polypropylene glycol mono(meth)acrylate (e.g., the number of propylene glycol units is 2 to 20);



poly(meth)acrylates of polyhydric alcohols such as  
ethylene glycol di(meth)acrylate,  
propylene glycol di(meth)acrylate,  
butylene glycol di(meth)acrylate, glycerin di(meth)acrylate,  
5 glycerin tri(meth)acrylate,  
pentaerythritol di(meth)acrylate,  
pentaerythritol tetra(meth)acrylate,  
1,4-cyclohexane diol di(meth)acrylate,  
polyethylene glycol di(meth)acrylate (e.g., the number of  
10 ethylene glycol units is 2 to 20), and  
polypropylene glycol di(meth)acrylate (e.g., the number of  
propylene glycol units is 2 to 20);

(poly)esters of non-polymerizable polybasic acids with  
hydroxylalkyl (meth)acrylates, such as  
15 mono[2-(meth)acryloyloxyethyl] succinate,  
di[2-(meth)acryloyloxyethyl] succinate,  
mono[2-(meth)acryloyloxyethyl] adipate,  
di[2-(meth)acryloyloxyethyl] adipate,  
mono[2-(meth)acryloyloxyethyl] phthalate, and  
20 di[2-(meth)acryloyloxyethyl] phthalate;

amino group-containing (meth)acrylates such as  
2-aminoethyl (meth)acrylate,  
2-(N-methylamino)ethyl (meth)acrylate,  
2-(N,N-dimethylamino)ethyl (meth)acrylate,  
25 2-(N-ethylamino)ethyl (meth)acrylate,  
2-(N,N-diethylamino)ethyl (meth)acrylate,  
3-(N,N-dimethylamino)propyl (meth)acrylate, and  
4-(N,N-dimethylamino)butyl (meth)acrylate; and

epoxy group-containing (meth)acrylates such as  
30 glycidyl (meth)acrylate.

[0031]

Examples of suitable (meth)acrylonitrile derivatives  
include  $\alpha$ -chloroacrylonitrile,  $\alpha$ -chloromethylacrylonitrile,  
 $\alpha$ -trifluoromethylacrylonitrile,  $\alpha$ -methoxyacrylonitrile,  
35  $\alpha$ -ethoxyacrylonitrile, and vinylidene cyanide. Examples of  
suitable (meth)acrylamide derivatives include

N-methyl(meth)acrylamide, N,N-dimethyl(meth)acrylamide, N-ethyl(meth)acrylamide, N,N-diethyl(meth)acrylamide, N-methoxy(meth)acrylamide, N,N-dimethoxy(meth)acrylamide, N-ethoxy(meth)acrylamide, N,N-diethoxy(meth)acrylamide, 5 diacetone (meth)acrylamide, N-methylol (meth)acrylamide, N-(2-hydroxyethyl)(meth)acrylamide, N,N-dimethylaminomethyl(meth)acrylamide, N-(2-dimethylamino)ethyl(meth)acrylamide, N,N'-methylenebis(meth)acrylamide, and 10 N,N'-ethylenebis(meth)acrylamide. Examples of suitable alkyl vinyl ethers include methyl vinyl ether, ethyl vinyl ether, butyl vinyl ether, and hexyl vinyl ether. Examples of suitable alkyl vinyl esters include vinyl formate, vinyl acetate, vinyl acrylate, vinyl lactate, vinyl caproate, and 15 vinyl stearate. Examples of styrene and derivatives thereof include styrene,  $\alpha$ -methylstyrene, and vinyl toluene. Of these monomers, (meth)acrylates are preferred. Especially preferred are methyl (meth)acrylate, ethyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, 20 n-hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, isononyl (meth)acrylate, cyclohexyl (meth)acrylate, 4-methylcyclohexyl (meth)acrylate, and 4-t-butylcyclohexyl (meth)acrylate.

[0032]

25 The above monomers may be used alone or in admixture of two or more. Of these monomer, copolymerizing an acrylic monomer having a cyclic hindered amine structure is preferred for improving photo-stability and weather resistance. The preferred content of the acrylic monomer is 30 0.1 to 10% by weight based on the copolymer composition because more than 10 wt% of the acrylic monomer can detract from adhesion of the coating.

[0033]

35 In the undercoating composition of the invention, the organic copolymer as the main component is comprised of (A) the benzotriazole based UV-absorbing vinyl monomer, (B) the alkoxysilyl group-containing vinyl monomer, and (C) the

other copolymerizable monomer, described above. The copolymer can be readily prepared by adding a radical polymerization initiator to a solution of the monomers, followed by heating to effect reaction. The initiator is  
5 selected from peroxides such as dicumyl peroxide and benzoyl peroxide and azo compounds such as azobisisobutyronitrile.

[0034]

Preferably the organic copolymer have a weight average molecular weight of 1,000 to 200,000.

10 [0035]

In the undercoating composition, an appropriate amount of the organic copolymer is 10 to 80% by weight. If the organic copolymer is less than 10% by weight, the primer coating composition may become thermoplastic and less  
15 resistant to heat. If the organic copolymer exceeds 80% by weight of the primer coating composition, adhesion may become poor.

[0036]

In the undercoating composition, a compound containing  
20 a nitrogen atom and an alkoxysilyl group in a molecule may be added to the above organic copolymer. Preferably the compound contains at least one nitrogen atom and at least two alkoxysilyl groups in a molecule. Preferred examples of the compound used herein include an amino group-containing  
25 alkoxysilane, amino group-containing di(alkoxysilane), amide group-containing alkoxysilane, one obtained by reacting an amino group-containing alkoxysilane with an epoxy group-containing alkoxysilane and a silylating agent and amidating the reaction product, the reaction product of an  
30 amino group-containing alkoxysilane with a (poly)(meth)acrylic compound, the reaction product of an amino group-containing alkoxysilane with a (meth)acrylic group-containing alkoxysilane, the reaction product of a polyamine compound with a (meth)acrylic group-containing  
35 alkoxysilane, and one obtained by reacting an amino group-containing alkoxysilane with a polyfunctional isocyanate compound and amidating the reaction product. Of

these, preferred is the one obtained by reacting an amino group-containing alkoxysilane with an epoxy group-containing alkoxysilane and a silylating agent and amidating the reaction product.

5        [0037]

Illustrative examples of the components used herein are described. Examples of the amino group-containing alkoxysilane include 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane,  
10 3-aminopropylmethyldimethoxysilane, 3-aminopropylmethyldiethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyltriethoxysilane, N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane,  
15 N-(2-aminoethyl)-3-aminopropylmethyldiethoxysilane, 3-(trimethoxysilylpropyl)aminopropyltrimethoxysilane, 3-(triethoxysilylpropyl)aminopropyltriethoxysilane, 2-(trimethoxysilylpropyl)aminoethyl-3-aminopropyltrimethoxysilane, and  
20 2-(triethoxysilylpropyl)aminoethyl-3-aminopropyltriethoxysilane.

[0038]

A typical amino group-containing di(alkoxysilane) is bis(trimethoxysilylpropyl)amine.

25        [0039]

Examples of the amide group-containing alkoxysilane include ureidopropyltrimethoxysilane, ureidopropyltriethoxysilane, ureidopropylmethyldimethoxysilane, and  
30 ureidopropylmethyldiethoxysilane.

[0040]

Examples of the (poly)(meth)acrylic compound include alkyl methacrylates such as methyl methacrylate, butyl methacrylate and 2-ethylhexyl methacrylate,  
35 alkyl acrylates such as methyl acrylate, ethyl acrylate and butyl acrylate, as well as acrylamide, acrylonitrile, and ethylene glycol dimethacrylate.

[0041]

Examples of the polyamine compound include ethylene diamine, diethylene triamine, triethylene triamine, tetraethylene pentamine, and piperazine.

5 [0042]

Examples of the polyisocyanate compound include toluene diisocyanate, diphenylmethane diisocyanate, hexamethylene diisocyanate, 2,2,4-trimethylhexamethylene diisocyanate, 10 2,4,4-trimethylhexamethylene diisocyanate, p-phenylene diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, 3,3'-dimethyldiphenyl-4,4'-diisocyanate, dianisidine diisocyanate, m-xylene diisocyanate, 15 isophorone diisocyanate, 1,5-naphthalene diisocyanate, trans-1,4-cyclohexyl diisocyanate, lysine diisocyanate, dimethyltriphenylmethane tetraisocyanate, triphenylmethane triisocyanate, and tris(phenyl isocyanate)thiophosphate.

20 [0043]

Examples of the (meth)acrylic group-containing alkoxysilane are as exemplified above for the alkoxysilyl group-containing acrylic monomer.

[0044]

25 The process of obtaining the amide compound by reacting an amino group-containing alkoxysilane with an epoxy group-containing alkoxysilane and a silylating agent and amidating the reaction product is described below. The amino group-containing alkoxysilane is as exemplified above 30 although N-(2-aminoethyl)-3-aminopropyltrimethoxysilane and N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane are preferred for adhesion and operation. The epoxy group-containing alkoxysilane used herein is not critical although  $\gamma$ -glycidoxypropyltrimethoxysilane, 35  $\gamma$ -glycidoxypropylmethyldimethoxysilane, and

$\beta$ -(3,4-epoxycyclohexyl)ethylmethyldimethoxysilane are preferred for reactivity and operation. Examples of the silylating agent include hexamethyldisilazane, N,N'-bis(trimethylsilyl)formamide and  
5 N,N'-bis(trimethylsilyl)urea. When the amino group-containing alkoxy silane reacts with the epoxy group-containing alkoxy silane, the silylating agent serves to protect the OH groups generated by the reaction for preventing reaction between OH groups and alkoxy silyl  
10 groups, thereby precluding a change with time of the reaction product.

[0045]

Reaction of the amino group-containing alkoxy silane with the epoxy group-containing alkoxy silane and the  
15 silylating agent may be effected by adding dropwise the epoxy group-containing alkoxy silane to a mixture of the amino group-containing alkoxy silane and the silylating agent and heating the mixture for reaction. Alternatively, the amino group-containing alkoxy silane is reacted with the  
20 epoxy group-containing alkoxy silane, and the silylating agent is added to the reaction product for further reaction.

[0046]

In this reaction, the amino group-containing alkoxy silane and the epoxy group-containing alkoxy silane are  
25 preferably used in such amounts that the molar ratio of epoxy groups to amino (=N-H) groups may range from 0.3/1 to 1.2/1. If the molar ratio of epoxy/amino is less than 0.3, only a less number of alkoxy groups per molecule participate in crosslinking, leading to short cure, and the entire  
30 molecule is not spread, leading to a weak surface bond. If the molar ratio of epoxy/amino is more than 1.2, amino (=N-H) groups which can be amidated during subsequent amidation step become few, exacerbating water-resistant bond.

35 [0047]

The reaction product is then amidated. For amidation, the reaction product may be reacted with a carboxylic acid

halide, acid anhydride or acid isopropenyl ester such as acetic chloride, acetic bromide, propionic chloride, acetic anhydride, isopropenyl acetate or benzoyl chloride.

[0048]

5 In the inventive undercoating composition, 0.1 to 50 parts, especially 0.5 to 20 parts by weight of the above compound is preferably blended per 100 parts by weight of the organic copolymer. More than 50 parts by weight of the compound sometimes results in a primer layer having a too  
10 high crosslinked density, a high hardness, and rather poor adhesion.

[0049]

Constituent components other than the reaction product in the undercoating composition are described.

15 [0050]

In the undercoating composition, a photo-stabilizer having at least one cyclic hindered amine structure in a molecule may be added for improving weather resistance. The photo-stabilizer used herein should preferably be fully  
20 soluble in the solvent of the primer coating composition, compatible with the organic copolymer, and low volatile.

[0051]

In the undercoating composition, 0.1 to 10 parts by weight of the photo-stabilizer is preferably blended per 100  
25 parts by weight of the organic copolymer. More than 10 parts of the photo-stabilizer detracts from adhesion of a coating.

[0052]

Illustrative examples of the photo-stabilizer include  
30 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidinyl)pyrrolidine-2,5-dione,  
N-methyl-3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidinyl)-pyrrolidine-2,5-dione,  
N-acetyl-3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidinyl)-  
35 pyrrolidine-2,5-dione,  
bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate,  
bis(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate,

tetrakis(2,2,6,6-tetramethyl-4-piperidyl)

1,2,3,4-butanetetracarboxylate,

tetrakis(1,2,2,6,6-pentamethyl-4-piperidyl) 1,2,3,4-butane-tetracarboxylate,

5 a condensate of 1,2,3,4-butanetetracarboxylic acid with 2,2,6,6-tetramethyl-piperidinol and tridecanol, 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro-[4,5]decane-2,4-dione,

a condensate of 1,2,3,4-butanetetracarboxylic acid with  
10 1,2,6,6-tetramethyl-4-piperidinol and

$\beta,\beta,\beta,\beta'$ -tetramethyl-3,9-(2,4,8,10-tetraoxaspiro[5,5]-undecane)diethanol, and a condensate of

1,2,3,4-butanetetracarboxylic acid with 2,2,6,6-tetramethyl-4-piperidinol and

15  $\beta,\beta,\beta,\beta'$ -tetramethyl-3,9-(2,4,8,10-tetraoxaspiro[5,5]-undecane)diethanol. For the purpose of fixing the photo-stabilizer, there may be also used silyl-modified photo-stabilizers as disclosed in JP-B 61-56187, for example, 2,2,6,6-tetramethylpiperidino-4-propyltrimethoxysilane,  
20 2,2,6,6-tetramethylpiperidino-4-propylmethyldimethoxysilane, 2,2,6,6-tetramethylpiperidino-4-propyltriethoxysilane, and 2,2,6,6-tetramethylpiperidino-4-propylmethyldiethoxysilane as well as (partial) hydrolyzates thereof. These photo-stabilizers may be used in admixture of two or more.

25 [0053]

In the undercoating composition, a conventional ultraviolet absorber which has not been silyl modified may be added insofar as no detrimental effect is exerted. Such UV-absorbers are organic UV-absorbers compatible with the  
30 organic copolymer. Derivatives of compounds having a hydroxybenzophenone, benzotriazole, cyanoacrylate or triazine main skeleton are especially preferred. Also acceptable are polymers such as vinyl polymers having such a UV-absorber incorporated on a side chain. Exemplary  
35 UV-absorbers are 2,4'-dihydroxybenzophenone, 2,2',4,4'-tetrahydroxybenzophenone, 2-hydroxy-4-methoxybenzophenone,



2-hydroxy-4-methoxybenzophenone-5-sulfonic acid,  
2-hydroxy-4-n-octoxybenzophenone,  
2-hydroxy-4-n-dodecyloxybenzophenone,  
2-hydroxy-4-n-benzyloxybenzophenone,  
5 2,2'-dihydroxy-4,4'-dimethoxybenzophenone,  
2,2'-dihydroxy-4,4'-diethoxybenzophenone,  
2,2'-dihydroxy-4,4'-dipropoxybenzophenone,  
2,2'-dihydroxy-4,4'-dibutoxybenzophenone,  
2,2'-dihydroxy-4-methoxy-4'-propoxybenzophenone,  
10 2,2'-dihydroxy-4-methoxy-4'-butoxybenzophenone,  
2,3,4-trihydroxybenzophenone,  
2-(2-hydroxy-5-t-methylphenyl)benzotriazole,  
2-(2-hydroxy-5-t-octylphenyl)benzotriazole,  
2-(2-hydroxy-3,5-di-t-butylphenyl)benzotriazole,  
15 ethyl-2-cyano-3,3-diphenyl acrylate,  
2-ethylhexyl-2-cyano-3,3-diphenyl acrylate,  
2-(2-hydroxy-4-hexyloxyphenyl)-4,6-diphenyltriazine,  
4-(2-acryloxyethyl)-2-hydroxybenzophenone polymer, and  
2-(2'-hydroxy-5'-methacryloxyethylphenyl)-2H-benzotriazole  
20 polymer. Of these, 2,2',4,4'-tetrahydroxybenzophenone is  
most preferred from the standpoints of compatibility with  
the primer coating composition and volatility. These  
organic UV-absorbers may be used in admixture of two or  
more.

25 [0054]

If the undercoating composition has a too low  
viscosity to apply and thus forms only a thin coating, an  
acrylic polymer may be added as a component capable of  
imparting flexibility without detracting from adhesion.  
30 Such useful acrylic polymers include  
poly(alkyl methacrylates) and poly(alkyl acrylates) such as  
poly(methyl methacrylate), poly(butyl methacrylate), and  
poly(butyl acrylate), and copolymers thereof. These acrylic  
polymers are effective for imparting flexibility to the  
35 primer coating composition without detracting from adhesion.

[0055]

The amount of the acrylic polymer added is desirably limited to 30% by weight or less based on the entire primer coating composition since more than 30% by weight of the acrylic polymer can preclude the composition from heat curing.

[0056]

On use, the undercoating composition is diluted with a solvent. Useful solvents include diacetone alcohol, propylene glycol monomethyl ether, ethylene glycol monomethyl ether, propylene glycol monoethyl ether, ethylene glycol monoethyl ether, isobutyl alcohol, isopropyl alcohol, n-butyl alcohol, n-propyl alcohol, acetone, methyl ethyl ketone, methyl isobutyl ketone, acetyl acetone, ethyl acetate, butyl acetate, xylene, and toluene. The primer coating composition is generally diluted with the solvent into a solution containing 5 to 10% by weight of the organic copolymer prior to use.

[0057]

The undercoating composition is applied to a surface of a plastic substrate, typically a plastic film, which has been cleaned, whereupon the diluting solvent is evaporated off at room temperature or elevated temperature, leaving a dry undercoat of 0.5 to 20  $\mu\text{m}$ , preferably 1 to 10  $\mu\text{m}$  thick. The organic solvent dilution should preferably have a viscosity of about 5 to 50 centistokes. A dilution with a viscosity of less than 5 centistokes would be difficult to form a thick coat whereas a dilution with a viscosity of more than 50 centistokes would be difficult to handle and apply. To the composition, a fluorine or silicone surfactant may be added for leveling of the coating, and a catalytic amount of a crosslinking/curing catalyst may also be added for accelerating cure.

[0058]

The plastic substrates such as plastic films and sheets with the cured coat of the undercoating composition of

the present invention are improved in initial adhesion, heat resistance, hot-water resistance, and weather resistance. A topcoat is formed on the primer layer with the known organopolysiloxane composition. For example, the known  
5 composition comprises a hydrolyzate or co-hydrolyzate of an organoxysilane of the following general formula (1):



10 wherein  $R^4$  is an alkyl group, aryl group, halogenated alkyl group, halogenated aryl group or alkenyl group of 1 to 10 carbon atoms, or an organic group having an epoxy, (meth)acryloxy, mercapto, amino or cyano group,  $R^5$  is hydrogen or a monovalent organic group of 1 to 10 carbon  
15 atoms and  $m$  is equal to 0, 1 or 2.

The top coat is formed by applying and heating the composition especially to 50-140°C to cure it. The resulting plastic article has the inventive undercoating composition layer applied at its surface. The top coat of  
20 the organopolysiloxane synergistically cooperates with the undercoat of the undercoating composition to accomplish high adhesion and abrasion resistance as well as excellent weather resistance and its stability due to tight fixation of the UV-absorber in the undercoat.

25 [0059]

In formula (1),  $R^4$  is an alkyl group, aryl group, halogenated alkyl group, halogenated aryl group or alkenyl group of 1 to 10 carbon atoms, or an organic group having an epoxy, (meth)acryloxy, mercapto, amino or cyano group.  
30 Examples include alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, hexyl, decyl and cyclohexyl; aryl groups such as phenyl and phenethyl; halogenated alkyl groups such as 3-chloropropyl, 3,3,3-trifluoropropyl, and 3,3,4,4,5,5,6,6,6-nonafluorohexyl; halogenated aryl groups  
35 such as p-chlorophenyl; alkenyl groups such as vinyl, allyl, 9-decenyl and p-vinylbenzyl; epoxy group-containing organic groups such as 3-glycidoxypropyl,

$\beta$ -(3,4-epoxycyclohexyl)ethyl and 9,10-epoxydecyl;  
(meth)acryloxy group-containing organic groups such as  
 $\gamma$ -methacryloxypropyl and  $\gamma$ -acryloxy; mercapto  
group-containing organic groups such as  $\gamma$ -mercaptopropyl and  
5 p-mercaptomethylphenylethyl; amino group-containing organic  
groups such as  $\gamma$ -aminopropyl and  
( $\beta$ -aminoethyl)- $\gamma$ -aminopropyl; and cyano group-containing  
organic groups such as  $\beta$ -cyanoethyl.

[0060]

10  $R^5$  is a hydrogen atom or an organic group having 1 to  
10 carbon atoms. The organic group exemplifies an alkyl  
group, alkenyl group, alkoxyalkyl group or acyl group. An  
alkyl group and acyl group are preferred. Examples include  
methyl group, ethyl group, propyl group, isopropyl group,  
15 butyl group, hexyl group, phenyl group, isopropenyl group,  
methoxyethyl group and acetyl group.

[0061]

Illustrative, non-limiting, examples of the silane  
compounds that satisfy the above conditions include  
20 trialkoxy or triacyloxysilanes such as  
methyltrimethoxysilane, methyltriethoxysilane,  
methyltris(2-methoxyethoxy)silane, methyltriacetoxysilane,  
methyltripropoxysilane, methyltriisopropenoxysilane,  
methyltributoxysilane, ethyltrimethoxysilane,  
25 ethyltriethoxysilane, vinyltrimethoxysilane,  
vinyltriethoxysilane, vinyltriacetoxysilane,  
vinyltris(2-methoxyethoxy)silane, vinyltriisopropenoxysilane,  
phenyltrimethoxysilane, phenyltriethoxysilane,  
phenyltriacetoxysilane,  $\gamma$ -chloropropyltrimethoxysilane,  
30  $\gamma$ -chloropropyltriethoxysilane,  $\gamma$ -chloropropyltripropoxysilane,  
3,3,3-trifluoropropyltrimethoxysilane,  
 $\gamma$ -glycidoxypropyltrimethoxysilane,  
 $\gamma$ -glycidoxypropylmethyldimethoxysilane,  
 $\gamma$ -glycidoxypropyltriethoxysilane,

- $\gamma$ -glycidoxypropylmethyldiethoxysilane,  
 $\beta$ -(3,4-epoxycyclohexyl)ethyltrimethoxysilane,  
 $\beta$ -(3,4-epoxycyclohexyl)ethylmethyldimethoxysilane,  
 $\beta$ -(3,4-epoxycyclohexyl)ethyltriethoxysilane,  
5  $\beta$ -(3,4-epoxycyclohexyl)ethylmethyldiethoxysilane,  
 $\gamma$ -methacryloxypropyltrimethoxysilane,  
 $\gamma$ -acryloxypropyltrimethoxysilane,  
 $\gamma$ -aminopropyltrimethoxysilane,  $\gamma$ -aminopropyltriethoxysilane,  
 $\gamma$ -mercaptopropyltrimethoxysilane,  
10  $\gamma$ -mercaptopropyltriethoxysilane,  
N-( $\beta$ -aminoethyl)- $\gamma$ -aminopropyltrimethoxysilane, and  
 $\beta$ -cyanoethyltrimethoxysilane;  
dialkoxysilanes or diacyloxysilanes such as  
dimethyldimethoxysilane, dimethyldiethoxysilane,  
15 dimethyldi(2-methoxyethoxy)silane, dimethyldiacetoxysilane,  
dimethyldipropoxysilane, dimethyldiisopropenoxysilane,  
dimethyldibutoxysilane, vinylmethyldimethoxysilane,  
vinylmethyldiethoxysilane, vinylmethyldiacetoxysilane,  
vinylmethyldi(2-methoxyethoxy)silane,  
20 vinylmethyldiisopropenoxysilane, phenylmethyldimethoxysilane,  
phenylmethyldiethoxysilane, phenylmethyldiacetoxysilane,  
 $\gamma$ -propylmethyldimethoxysilane,  $\gamma$ -propylmethyldiethoxysilane,  
 $\gamma$ -propylmethyldipropoxysilane,  
3,3,3-trifluoropropylmethyldimethoxysilane,  
25  $\gamma$ -methacryloxypropylmethyldimethoxysilane,  
 $\gamma$ -acryloxypropylmethyldimethoxysilane,  
 $\gamma$ -aminopropylmethyldimethoxysilane,  
 $\gamma$ -aminopropylmethyldiethoxysilane,  
 $\gamma$ -mercaptopropylmethyldimethoxysilane,  
30  $\gamma$ -mercaptopropylmethyldiethoxysilane,  
N-( $\beta$ -aminoethyl)- $\gamma$ -aminopropylmethyldimethoxysilane, and  
 $\beta$ -cyanoethylmethyldimethoxysilane; and

tetraalkoxysilanes such as methyl silicate, ethyl silicate, n-propyl silicate, n-butyl silicate, sec-butyl silicate, and t-butyl silicate.

[0062]

5 (Co-)hydrolyzates of these silane compounds are also useful. These silane compounds and/or (co-)hydrolyzates thereof may be used alone or in admixture of two or more.

[0063]

10 The (co-)hydrolyzates of the above silane compounds are obtained, for example, by adding water to a lower alcohol solution of the silane compound(s) in the presence of an acid catalyst. Exemplary lower alcohols are methanol, ethanol, isopropanol and butanol. Solvents compatible with these alcohols include ketones such as acetone and  
15 acetylacetone, esters such as ethyl acetate and isobutyl acetate, and ethers such as propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, and diisopropyl ether.

[0064]

20 For improving mar resistance, it is preferred to apply a colloidal silica-laden organopolysiloxane composition in which 5 to 70% by weight of colloidal silica (obtained by dispersing silica fines having a particle size of about 1 to 100 mμ in water or an alcohol such as methanol, ethanol,  
25 isobutanol or diacetone alcohol) is added to the above organopolysiloxane composition. Also a metal oxide such as titanium oxide, zirconium oxide, tin oxide or tungsten oxide may be added as a UV-shielding agent to the above organopolysiloxane composition. Moreover, a curing catalyst  
30 may be added in a catalytic amount to the above organopolysiloxane composition. The curing catalyst is selected from quaternary ammonium salts, alkali metal salts of organic acids, alkoxides and chelates of aluminum, titanium, chromium and iron, perchlorates, acid anhydrides,  
35 polyamines, and Lewis acids, though not limited thereto.

[0065]

The undercoating composition is useful in various plastic materials. Specifically, the plastic materials to which the composition is applicable preferably include those of polycarbonate, polystyrene, modified acrylic resins, urethane resins, thiourethane resins, polycondensates of halogenated bisphenol A and ethylene glycol, acrylic urethane resins, halogenated aryl group-containing acrylic resins, and sulfur-containing resins.

[0066]

Synthesis Examples, Examples and Comparative Examples of the invention are given below by way of illustration and not by way of limitation. All parts and percents are by weight.

[0067]

<Synthesis of alkoxysilyl group-containing, UV-absorbing organic copolymers>

[Synthesis Example 1]

A 2-liter flask equipped with a stirrer, condenser and thermometer was charged with 376.7 g of diacetone alcohol as a solvent, which was heated at 80°C under a nitrogen stream. To the flask were successively admitted a 90-g portion of a monomer premix consisting of 16.5 g of 2-[2'-hydroxy-5'-(2-methacryloxyethyl)phenyl]-2H-benzotriazole, 54 g of  $\gamma$ -methacryloxypropyltrimethoxysilane, 216 g of methyl methacrylate, 16.9 g of ethyl acrylate, 16.9 g of vinyl acetate, and 33.8 g of glycidyl methacrylate, and a 36-g portion of a solution of 2.3 g of 2,2'-azobis(2-methylbutyronitrile) as a polymerization initiator in 177.7 g of diacetone alcohol. Reaction was effected at 80°C for 30 minutes, following which the remainder of the monomer premix and the remainder of the polymerization initiator solution were simultaneously added dropwise at 80 to 90°C over 1.5 hours. Stirring was continued for a further 5 hours at 80 to 90°C.

[0068]

The resulting solution of alkoxysilyl group-containing, UV-absorbing organic copolymer had a viscosity of 14,000 centipoise. The copolymer had a UV-absorbing monomer content of 4.7% and an alkoxyl group-containing monomer content of 15.2%. It had a weight average molecular weight of 105,000 on GPC analysis using standard polystyrene as a reference.

[0069]

10 [Synthesis Example 2]

A solution of alkoxysilyl group-containing, UV-absorbing organic copolymer was prepared as in Synthesis Example 1 except that 376.7 g of diacetone alcohol as the solvent was changed to 385.4 g, 16.5 g of 2-[2'-hydroxy-5'-(2-methacryloxyethyl)phenyl]-2H-benzotriazole as the monomer was changed to 35 g, and 2.8 g of 1,2,2,6,6-pentamethyl-4-piperidinyl methacrylate was used as an additional monomer.

[0070]

The resulting copolymer solution had a viscosity of 7,500 centipoise. The copolymer had a UV-absorbing monomer content of 9.3% and an alkoxyl group-containing monomer content of 14.3%. It had a weight average molecular weight of 96,400 on GPC analysis using standard polystyrene as a reference.

25 [0071]

[Synthesis Example 3]

A 2-liter flask equipped with a stirrer, condenser and thermometer was charged with 471.3 g of diacetone alcohol as a solvent and 55.2 g of 2-[2'-hydroxy-5'-(2-methacryloxyethyl)phenyl]-2H-benzotriazole, which were heated at 80°C under a nitrogen stream. To the flask were successively admitted a 90-g portion of a monomer premix consisting of 40.0 g of 2-[2'-hydroxy-5'-(2-methacryloxyethyl)phenyl]-2H-benzotriazole, 54 g of  $\gamma$ -methacryloxypropyltrimethoxysilane, 216 g of methyl methacrylate, 16.9 g of ethyl acrylate, 16.9 g of vinyl acetate, 33.8 g of glycidyl methacrylate, and 2.8 g of 1,2,2,6,6-pentamethyl-4-piperidinyl methacrylate, and a



36-g portion of a solution of 2.3 g of 2,2'-azobis(2-methylbutyronitrile) as a polymerization initiator in 177.7 g of diacetone alcohol. Reaction was effected at 80°C for 30 minutes, following which the remainder of the monomer premix and the remainder of the polymerization initiator solution were simultaneously added dropwise at 80 to 90°C over 1.5 hours. Stirring was continued for a further 5 hours at 80 to 90°C.

[0072]

10       The resulting solution of alkoxysilyl group-containing, UV-absorbing organic copolymer had a viscosity of 10,700 centipoise. The copolymer had a UV-absorbing monomer content of 22.0% and an alkoxyl group-containing monomer content of 12.3%. It had a weight average molecular weight of 58,000 on GPC analysis using standard polystyrene as a reference.

[0073]

[Synthesis Example 4]

20       A solution of alkoxysilyl group-containing, UV-absorbing organic copolymer was prepared as in Synthesis Example 1 except that 16.5 g of 2-[2'-hydroxy-5'-(2-methacryloxyethyl)phenyl]-2H-benzotriazole as the monomer was changed to 0.2 g, and 216 g of methyl methacrylate was changed to 232.3 g.

25       [0074]

      The resulting copolymer solution had a viscosity of 13,200 centipoise. The copolymer had a UV-absorbing monomer content of 0.06% and an alkoxyl group-containing monomer content of 15.2%. It had a weight average molecular weight of 99,900 on GPC analysis using standard polystyrene as a reference.

[0075]

[Synthesis Example 5]

35       A solution of alkoxysilyl group-containing, UV-absorbing organic copolymer was prepared as in Synthesis Example 1 except that 16.5 g of 2-[2'-hydroxy-5'-(2-methacryloxyethyl)phenyl]-2H-benzotriazole as the monomer

was changed to 194.8 g, and 216 g of methyl methacrylate was changed to 37.7 g. The monomer premix then became slurry because 2-[2'-hydroxy-5'-(2-methacryloxyethyl)phenyl]-2H-benzotriazole was not fully dissolved.

5 [0076]

The resulting copolymer solution had a viscosity of 3,400 centipoise. The copolymer had a UV-absorbing monomer content of 55.0% and an alkoxyl group-containing monomer content of 15.2%. It had a weight average molecular weight  
10 of 32,000 on GPC analysis using standard polystyrene as a reference.

[0077]

[Synthesis Example 6]

A solution of UV-absorbing organic copolymer was  
15 prepared as in Synthesis Example 1 except that 54 g of  $\gamma$ -methacryloxypropyltrimethoxysilane was omitted, and 216 g of methyl methacrylate was changed to 270 g.

[0078]

The resulting copolymer solution had a viscosity of  
20 38,000 centipoise. The copolymer had a UV-absorbing monomer content of 4.7% and an alkoxyl group-containing monomer content of 0%. It had a weight average molecular weight of 94,000 on GPC analysis using standard polystyrene as a reference.

25 [0079]

<Synthesis of compounds containing a nitrogen atom and an alkoxysilyl group in a molecule>

[Synthesis Example 7]

A 2-liter flask equipped with a stirrer, condenser and  
30 thermometer was charged with 222 g of N-2-(aminoethyl)-3-aminopropyltrimethoxysilane and 242 g of hexamethyldisilazane as a silylating agent. The contents were heated at 120°C under a nitrogen stream. To the flask, 496 g of  $\gamma$ -glycidoxypropylmethyldiethoxysilane was added dropwise for  
35 reaction. The reaction mixture was further stirred and heated at 120°C for 5 hours. A low-boiling fraction was stripped off at 100°C under vacuum, leaving 862 g of a

viscous compound having a viscosity of 1,387 centistokes, a refractive index of 1.4618 and a specific gravity of 1.048.

[0080]

Next, a 2-liter flask equipped with a stirrer,  
5 condenser and thermometer was charged with 862 g of the reaction product and 862 g of toluene. In a nitrogen stream, 141 g of acetic anhydride was added dropwise to the flask at room temperature for reaction. The reaction mixture was further stirred and heated at 110°C for 2 hours.  
10 Methanol, 141 g, was added dropwise to the reaction mixture at 50°C, which was further stirred and heated at 50°C for 1 hour. A low-boiling fraction was stripped off at 100°C under vacuum, leaving a highly viscous compound.

[0081]

15 This compound was analyzed by IR absorption spectroscopy, finding no absorption peaks attributable to the OH or NH group in the region of at least 3,000  $\text{cm}^{-1}$ , but a definite peak attributable to the amide group absorption at 1,650  $\text{cm}^{-1}$ .

20 [0082]

<Synthesis of colloidal silica-laden organopolysiloxane composition>

[Synthesis Example 8]

A 1-liter flask equipped with a stirrer, condenser and  
25 thermometer was charged with 164 g of methyltriethoxysilane and 46 g of isobutanol, which were maintained below 5°C under ice cooling with stirring. To this was added 138 g of colloidal silica (containing 20% of  $\text{SiO}_2$ ) below 5°C. The mixture was stirred for 2 hours under ice cooling and for a  
30 further 8 hours at 20 to 25°C. Thereafter, 45 g of diacetone alcohol and 50 g of isobutanol were added, 1.5 g of a 10% aqueous solution of sodium propionate was then added, and the resulting mixture was adjusted to pH 6 to 7 with acetic acid. This was adjusted with isobutanol to a  
35 nonvolatile content of 17% as measured by JIS K-6833 and ripened for 5 days at room temperature. The resulting colloidal silica-laden organopolysiloxane composition had a

viscosity of about 5 centistokes and the nonvolatile component had a number average molecular weight of about 1,000.

[0083]

5 [Synthesis Example 9]

The procedure of Synthesis Example 8 was repeated except that 3.0 g of a 10% aqueous solution of tetramethylammonium benzoate was used instead of the sodium propionate aqueous solution, obtaining a colloidal  
10 silica-laden organopolysiloxane composition.

[0084]

[Synthesis Example 10]

The procedure of Synthesis Example 8 was repeated except that there was further added 1.8 g of  
15 2,2',4,4'-tetrahydroxybenzophenone (corresponding to 2 parts per 100 parts of the solids of the colloidal silica-laden organopolysiloxane composition), obtaining a colloidal silica-laden organopolysiloxane composition.

[0085]

20 <Synthesis of silyl-modified photo-stabilizer>

[Synthesis Example 11]

A 0.3-liter flask equipped with a stirrer, condenser and thermometer was charged with 100 g (0.5 mol) of 2,2,6,6-tetramethyl-4-allyl-piperidine and 0.13 g of a  
25 butanol solution of chloroplatinic acid (2% solution of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ). To the flask at room temperature, 80.6 g (0.66 mol) of trimethoxysilane was added dropwise over one hour, and reaction effected at 90°C for 5 hours. At the end of reaction, distillation was effected under vacuum, collecting  
30 126 g of a fraction at 151-154°C at 7 mmHg. By gas chromatography, 2,2,6,6-tetramethylpiperidino-4-propyltrimethoxysilane was collected at a purity of 97%. Its structure was confirmed by IR spectrometry and proton-NMR analysis.

35 [0086]

Examples of the invention are given below by way of illustration. The abbreviations for UV-absorbers, hindered

amine photo-stabilizers, and organic copolymers used in Examples and Comparative Examples have the following meaning.

<Alkoxysilyl group-containing, UV-absorbing organic copolymers>

- 5 Pol-1: the reaction product of Synthetic Example 1  
Pol-2: the reaction product of Synthetic Example 2  
Pol-3: the reaction product of Synthetic Example 3  
Pol-4: the reaction product of Synthetic Example 4  
Pol-5: the reaction product of Synthetic Example 5  
10 Pol-6: the reaction product of Synthetic Example 6

<UV-absorbers>

- UVA-1: 2,2',4,4'-tetrahydroxybenzophenone  
UVA-2: 2-(3,5-di-t-butyl-2-hydroxyphenyl)-5-chlorobenzo-  
triazole  
15 UVA-3: 2-(2-hydroxy-4-hexyloxyphenyl)-4,6-diphenyltriazine  
UVA-4: a copolymer of 2-(2'-hydroxy-5'-methacryloxyethyl-  
phenyl)-2H-benzotriazole (30%) and methyl  
methacrylate (70%)  
UVA-5: a copolymer of 2-(2'-hydroxy-5'-methacryloxyethyl-  
20 phenyl)-2H-benzotriazole (30%) and styrene (70%)

<Hindered amine photo-stabilizers>

- HALS-1: N-acetyl-3-dodecyl-1-(2,2,6,6-tetramethyl-4-  
piperidinyl)pyrrolidine-2,5-dione  
HALS-2: a condensate of 1,2,3,4-butanetetracarboxylic acid,  
25 2,2,6,6-tetramethyl-piperidinol and tridecanol  
HALS-3: 2,2,6,6-tetramethylpiperidino-4-propyltrimethoxy-  
silane synthesized in Synthesis Example 11

<Compounds containing nitrogen and alkoxysilyl group in molecule>

- NSi-1: ureidopropyltriethoxysilane  
30 NSi-2: the reaction product of Synthetic Example 7

<Colloidal silica-laden organopolysiloxane compositions>

- HC-1: colloidal silica-laden organopolysiloxane composition  
of Synthetic Example 8  
HC-2: colloidal silica-laden organopolysiloxane composition  
35 of Synthetic Example 9  
HC-3: colloidal silica-laden organopolysiloxane composition  
of Synthetic Example 10

[0087]

In Examples, physical properties were measured and rated by the following procedures.

(1) Weathering test

5       An accelerated weathering test was carried out by a carbon arc sunshine weatherometer according to JIS K-5400. After 5,000 hours, a yellowing factor and adhesion were examined according to JIS K-7103. The adhesion is evaluated by the method shown below.

10      (2) Marring test

      Using a Taber abrader equipped with an abrasive wheel CS-10F, a sample was rotated under a load of 500 g according to ASTM 1044. After 1,000 revolutions, the sample was measured for haze. A Taber abrasion (%) was calculated as  
15      the haze after test minus the haze prior to test.

(3) Adhesion of cured film

      An adhesive tape test was carried out according to JIS K-5400 by scribing a sample with a razor along eleven spaced 1-mm apart orthogonal lines to define 100 square sections in  
20      the coating, closely applying a commercially available adhesive tape thereto, and quickly peeling the adhesive tape by an angle of 90 degrees. The number (X) of remaining (not peeled) coating sections is expressed as X/100.

[0088]

25      [Examples 1-12 and Comparative Examples 1-10]

      Undercoating compositions (A) to (V) were prepared according to the formulation shown in Tables 1 to 4 by mixing the alkoxysilyl group-containing, UV-absorbing organic copolymer (Pol-1 to 6) prepared in Synthetic  
30      Examples 1 to 6, polymethyl methacrylate having an average molecular weight of 150,000, the compound containing nitrogen and alkoxysilyl group in molecule (NSi-1, 2), the UV-absorber (UVA-1 to 5), and the photo-stabilizer (HALS-1 to 3), and diluting the mixture with a 20/80 mixture of  
35      diacetone alcohol and ethylene glycol monomethyl ether to a concentration of 10% organic copolymer solids.

[0089]

The undercoating composition was applied onto a cleaned surface of a polycarbonate resin sheet of 0.5 mm thick by the flow coating method and cured at about 120°C for about 30 minutes, obtaining a cured primer coating of 0.5 to 20  $\mu\text{m}$  thick. The colloidal silica-laden organopolysiloxane coating composition each obtained in Synthetic Examples 8 to 10 was applied onto the primer coating by the flow coating method and cured at about 120°C for about one hour, obtaining a cured coating of 0.5 to 20  $\mu\text{m}$  thick. The thus surface-coated sheets were examined for physical properties, with the results shown in Table 5.

[0090]

Table 1

	Example					
	1	2	3	4	5	6
Primer designation	A	B	C	D	E	F
UVA	-	-	-	-	-	-
Organic copolymer	Pol-1 (100 parts)	Pol-2 (100 parts)	Pol-3 (100 parts)	Pol-1 (100 parts)	Pol-1 (100 parts)	Pol-1 (100 parts)
Polymethyl methacrylate	-	-	-	-	20 parts	20 parts
NSi	-	-	-	-	NSi-1 (5 parts)	NSi-2 (20 parts)
HALS	-	-	-	-	HALS-1 (10 parts)	HALS-2 (10 parts)
Colloidal silica-laden organopolysiloxane	HC-1	HC-1	HC-1	HC-2	HC-1	HC-1

5 [0091]

Table 2

	Example					
	7	8	9	10	11	12
Primer designation	G	H	I	J	K	L
UVA	-	UVA-1 (3 parts)	UVA-2 (3 parts)	UVA-3 (3 parts)	UVA-4 (3 parts)	UVA-5 (3 parts)
Organic copolymer	Pol-2 (100 parts)	Pol-1 (100 parts)	Pol-1 (100 parts)	Pol-1 (100 parts)	Pol-1 (100 parts)	Pol-1 (100 parts)
Polymethyl methacrylate	20 parts	-	-	-	20 parts	-
NSi	NSi-2 (30 parts)	NSi-2 (20 parts)	NSi-2 (20 parts)	NSi-2 (20 parts)	NSi-2 (20 parts)	NSi-2 (20 parts)
HALS	HALS-3 (6 parts)	HALS-1 (3 parts)	HALS-3 (10 parts)	HALS-3 (6 parts)	HALS-1 (2 parts)	HALS-1 (2 parts)
Colloidal silica-laden organopolysiloxane	HC-3	HC-3	HC-3	HC-3	HC-3	HC-3



[0092]

Table 3

	Comparative Example					
	1	2	3	4	5	6
Primer designation	M	N	O	P	Q	R
UVA	-	UVA-1 (20 parts)	UVA-2 (20 parts)	UVA-3 (20 parts)	UVA-4 (20 parts)	UVA-5 (20 parts)
Organic copolymer	Pol-4 (100 parts)	Pol-4 (100 parts)	Pol-4 (100 parts)	Pol-4 (100 parts)	Pol-4 (100 parts)	Pol-4 (100 parts)
Polymethyl methacrylate	-	-	-	-	-	-
Ns1	-	-	-	-	-	-
HALS	-	-	-	-	-	-
Colloidal Silica-laden organopolysiloxane	HC-1	HC-1	HC-1	HC-1	HC-1	HC-1

5

[0093]

Table 4

	Comparative Example			
	7	8	9	10
Primer designation	S	T	U	V
UVA	UVA-1 (20 parts)	-	UVA-2 (20 parts)	-
Organic copolymer	Pol-4 (100 parts)	Pol-5 (100 parts)	Pol-5 (100 parts)	Pol-6 (100 parts)
Polymethyl methacrylate	20 parts	-	20 parts	-
NS1	NS1-2 (20 parts)	-	NS1-2 (20 parts)	-
HALS	HALS-2 (1 part)	-	HALS-2 (1 part)	-
Colloidal silica-laden organopolysiloxane	HC-1	HC-2	HC-2	HC-2

[0094]

**Table 5**

	Initial		Weathering	
	Yellowing factor	Taber abrasion	Yellowing factor	Adhesion
Example 1	1.0	7	2.0	100/100
Example 2	1.5	7	2.0	100/100
Example 3	1.5	8	1.5	100/100
Example 4	1.0	8	2.0	100/100
Example 5	1.5	7	2.5	100/100
Example 6	1.0	7	2.0	100/100
Example 7	1.0	8	2.0	100/100
Example 8	3.0	9	2.0	100/100
Example 9	1.0	8	2.0	100/100
Example 10	2.5	9	2.5	100/100
Example 11	1.0	8	2.0	100/100
Example 12	1.0	8	1.0	100/100
Comparative Example 1	1.0	9	35.0	100/100
Comparative Example 2	4.0	20	15.0	0/100
Comparative Example 3	1.5	15	8.0	0/100
Comparative Example 4	3.0	11	20.0	100/100
Comparative Example 5	1.5	10	10.0	100/100
Comparative Example 6	1.5	12	13.0	100/100
Comparative Example 7	1.5	8	9.0	100/100
Comparative Example 8	1.0	16	4.0	0/100
Comparative Example 9	1.5	18	4.0	50/100
Comparative Example 10	1.0	20	10.0	0/100

[0095]

[Effect of the Invention]

Coated plastic articles, especially of polycarbonate resins, having coatings of the inventive undercoating  
5 compositions are endowed with improved transparency, mar resistance, weather resistance and chemical resistance. They are suited on outdoor use, for example, as windows and windshields on automobiles, aircraft and other transporting vehicles, building windows, and acoustic barrier walls along  
10 highways.



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[ABSTRACT]

[Means for Solution]

5 An undercoating composition comprising an organic copolymer comprising (A) a UV-absorbing benzotriazole based vinyl monomer, (B) an alkoxysilyl group-containing vinyl monomer, and (C) another copolymerizable monomer, the alkoxysilyl group-containing vinyl monomer accounting for 0.1 to 50% by weight of the copolymer.

[Effect]

10 Coated plastic articles, especially of polycarbonate resins, having coatings of the inventive undercoating compositions are endowed with improved transparency, mar resistance, weather resistance and chemical resistance. They are suited on outdoor use, for example, as windows and windshields on automobiles,  
15 aircraft and other transporting vehicles, building windows, and acoustic barrier walls along highways.

[Selected Drawing] none